

BEST AVAILABLE COPY

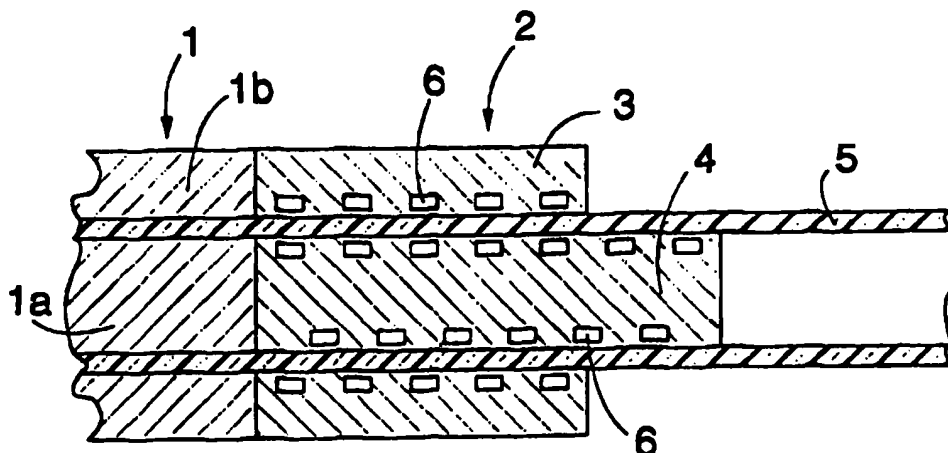
PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : B29C 47/88	A1	(11) International Publication Number: WO 97/10940 (43) International Publication Date: 27 March 1997 (27.03.97)
(21) International Application Number: PCT/FI96/00502 (22) International Filing Date: 20 September 1996 (20.09.96) (30) Priority Data: 9503272-8 20 September 1995 (20.09.95) SE PCT/EP96/02801 26 June 1996 (26.06.96) WO (34) Countries for which the regional or international application was filed: US et al. (71) Applicant (for all designated States except US): UPONOR B.V. [NL/NL]; Hoeckenrode 6-8, NL-1102 BR Amsterdam (NL). (72) Inventors; and (75) Inventors/Applicants (for US only): JÄRVENKYLÄ, Jyri [FI/FI]; Tapiontie 4, FIN-15870 Hollola (FI). LAHTINEN, Terho [FI/FI]; Sotkatie 1 A 4, FIN-00200 Helsinki (FI). SJÖBERG, Michael [SE/SE]; Guonilbogatan 22 B, S-723 40 Västerås (SE). (74) Agent: OY KOLSTER AB; Iso Roobertinkatu 23, P.O. Box 148, FIN-00121 Helsinki (FI).	(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published With international search report. In English translation (filed in Finnish).	

(54) Title: METHOD AND APPARATUS FOR MAKING AN EXTRUSION PRODUCT, AND AN EXTRUSION PRODUCT



(57) Abstract

The invention relates to an extruder with which material is extruded through a tool (2). Fluoropolymer is used between the extrusion material and the tool (2) for reducing friction between the material and the tool. At least the surface of the tool (2) against fluoropolymer is of a material whose thermal conductivity is greater than the thermal conductivity of ordinary tool steel. Therefore the friction heat generated can be conducted efficiently away from the interface between the tool (2) and the extrusion material towards the tool (2), whereby the wear of fluoropolymer can be reduced and thus the durability of the tool (2) can be improved. In that case the extrusion product will slip evenly out from the tool (2), whereby the surface of the product is essentially smooth without transverse microscopic stripes repeated at a specific wave length.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LJ	Liechtenstein	SJ	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

WO 97/10940

PCT/FI96/00502

1

Method and apparatus for making an extrusion product,
and an extrusion product

5 The present invention relates to a method for
making an extrusion product, in which method an
extrusion material is extruded by an extruder from its
extrusion portion through a tool and fluoropolymer is
used between the extrusion material and the tool for
10 reducing friction between the extrusion material and
the tool.

 The present invention further relates to an
apparatus for making an extrusion product, which
apparatus comprises an extrusion portion for extruding
an extrusion material and a tool through which the
15 extrusion material is extruded and fluoropolymer is
arranged to be used between the extrusion material and
the tool as a slip agent.

 The present invention also relates to a
product made with the method.

20 It is essential in the production of
crosslinked polyethylene, for example, that the
material will flow well against the walls of the tool
situated after the screw of the extruder in such a
manner that the friction heat generated therein would
25 remain so low that crosslinking cannot start too early.
The kinds of polyethylene suitable for producing
crosslinked pipes, for example, flow very badly on
account of their high molecular weight. On account of
low extrusion heat and great viscosity mentioned above,
30 the extrusion process is rather abrupt so that the
temperature of the screw and of the cylinder will
easily rise too high because of the generated friction
heat.

 In plastic industry extrusion tools are mainly
35 manufactured of easily machineable hard tool steel or

WO 97/10940

PCT/FI96/00502

2

possibly of stainless steel. In order to improve wear resistance required for cleaning processes, for instance, tools are generally chrome plated. EP 0 507 613 discloses that a tool is coated with polytetrafluoroethylene. Polytetrafluoroethylene reduces friction very efficiently and the plastic material will slip steadily along the surface of the tool on account of it. When machining plastics with a high molecular weight, polytetrafluoroethylene will wear off very fast from the surface of the tool during the extrusion process. Therefore it is necessary to halt the extrusion process for adding a new polytetrafluoroethylene layer to the tool. This re-coating has to be carried out even daily. Thus halting the process and starting it again, and wear and addition process of polytetrafluoroethylene will easily raise the costs considerably high. Excessive wear of polytetrafluoroethylene can easily be seen in the final product, too, as the quality of the surface suffers easily. Typically the inner surface of the pipe can become coarse or plastic fluff can be found there. Poor characteristics are not necessarily visible in the outer surface of the pipe, but in microscopic measuring unevenness will become evident.

WO 94/21441 puts forth a solution to the above-mentioned problem where instead of using polytetrafluoroethylene, a layer of a sacrificial thermosetting material is extruded between the extrusion product and the tool. As in most cases the layer will have to be removed from the surface of the product after extrusion, the invention is complicated and difficult to realize.

WO 92/11125 discloses that a slip agent is added to a plastic material. However, if the slip agent is added to a product which has a high molecular

WO 97/10940

PCT/F196/00502

3

weight, for example, and which requires strong machining, it will result in that on account of its slipperiness, the plastic material will easily become disengaged from the screw in melting zone and the plastic material will come out of the extruder unmolten.

The object of the present invention is to provide a method and an apparatus for making an extrusion product where the disadvantages mentioned above can be avoided. A further object is to provide an extrusion product with good characteristics.

The method according to the invention is characterized in that at least the surface of the tool against fluoropolymer is of a material whose thermal conductivity is greater than the thermal conductivity of ordinary tool steel, whereby the friction heat generated can be conducted efficiently away from the interface between the tool and the extrusion material towards the tool.

Further, the apparatus according to the invention is characterized in that at least the surface of the tool against fluoropolymer, at least partly at the smallest cross-section, is of a material whose thermal conductivity is greater than the thermal conductivity of ordinary tool steel.

In addition, the product made with the method according to the invention is characterized in that the surface of the product is essentially smooth without any transverse microscopic stripes repeated at a specific wave length.

The essential idea of the invention is that there is fluoropolymer, such as polytetrafluoroethylene, between the tool and the plastic material to be extruded for reducing friction between the plastic material and the tool and that at least the surface of

WO 97/10940

PCT/FI96/00582

4

the tool against fluoropolymer is of a material whose thermal conductivity is greater than the thermal conductivity of ordinary tool steel, whereby the friction heat generated can be conducted fast away from the interface towards the tool. A further idea of one preferred embodiment is that there is a wear resistant coating on the surface of the tool, such as DLC, which comprises pores filled with a fluoro compound, such as polytetrafluoroethylene. The idea of a second preferred embodiment is that there is a slip agent layer essentially comprising a fluoro compound between the coating of the tool and the plastic material. Most preferably the intermediate layer comprises at least partly a fluoro compound, such as fluoro-elastomer, which is supplied into the plastic, and which migrates to abutment surfaces. The idea of a third embodiment is that the fluoro compound forming the slip agent is extruded between the plastic layer and the tool primarily after plastic melting zone just before the nozzle of the tool.

The advantage of the invention is that when at least the surface of the tool is of a material that conducts heat well, the friction heat generated can be conducted efficiently away from the interface of the plastic material to be extruded and the tool, whereby temperature control of the tool will be very good and the temperature will not rise even at the interface too high for polytetrafluoroethylene, for example. It has been unexpectedly found out that by conducting heat away from the interface, the wear resistance of polytetrafluoroethylene, for example, has been considerably improved. In an ordinary tool, although the temperature of the tool is adjusted e.g. to 250°C, polytetrafluoroethylene will wear rather easily from it even though the melting temperature of polytetrafluoro-

WO 97/10940

PCT/FI96/00502

5

ethylene is more than 300°C. Because of friction, the temperature at the interface exceeds the highest temperature allowed for polytetrafluoroethylene, wherefore polytetrafluoroethylene will wear off easily.

5 By means of the method according to the invention, temperature is prevented from rising too high at the interface and thus wear resistance of the tool will improve. DLC is very wear resistant and when its pores are filled with a fluoro compound, the friction between

10 the tool and the plastic material to be extruded will be very small. By forming a slip agent layer between the abutment surfaces of the tool and the plastic material, the material can slip very well along the surface of the tool, but the slip agent layer does not

15 disturb the machining of the actual plastic material, whereby the plastic material may be crosslinked polyethylene that is difficult to machine. By supplying the slip agent between the plastic material to be extruded and the tool primarily after plastic melting

20 zone, the friction heat can also be utilized very efficiently in the melting and machining zone of the actual plastic material.

The invention will be explained in more detail in the accompanying drawings, in which

25 Figure 1 shows a schematic cross-sectional side view of one apparatus according to the invention,

Figure 2 shows a schematic cross-sectional side view of a second apparatus according to the invention,

30 Figure 3 shows a schematic cross-sectional side view of a third apparatus according to the invention, and

Figure 4a shows a measuring result from the surface of a pipe of an unsatisfactory quality,

35 Figure 4b illustrates Fourier analysis of the

WO 97/10940

PCT/FI96/00502

6

measuring according to Figure 4a,

Figure 5a shows a measuring result of the surface of a pipe made with the method according to the invention, and

5 Figure 5b illustrates Fourier analysis of the measuring according to Figure 5a.

Only the end portion of an extruder portion 1 of an extruder is shown in the appended figure for the sake of clarity in such a manner that the end of a screw portion 1a of the extruder portion 1 and the end of a cylinder portion 1b are visible in the figure. The extruder may be any extruder known per se, an ordinary screw extruder, for example. A tool 2 is arranged to the end of the extruder portion 1. The tool 2 comprises a nozzle outside the extrusion product and a mandrel 4 inside it. The tool 2 can be of any ordinary type, such as a tool having a mandrel carrier provided with a spiral divider, a so-called basket die-head tool having a perforated supporter, a tool having a mandrel carrier secured to the head of a screw, or a so-called crosshead tool. These detailed features have been omitted from the appended figures for the sake of clarity. The extrusion product, a pipe 5 for example, is extruded from between the nozzle 3 and the mandrel 4. The extrusion product can be in addition to the pipe 5 a cable sheath or a film or any such product.

10 The surfaces of the tool 2 against the plastic material to be extruded are coated with fluoroplastic, most preferably with polytetrafluoroethylene for attaining as good slip characteristics as possible. Before polytetrafluoroethylene is coated, the surfaces of the tool are applied a material whose thermal conductivity is better than that on the other parts of the tool 2 in case the tool 2 is manufactured of tool steel, for example. Thermal conductivity of tool steel

15

20

25

30

35

WO 97/10940

PCT/FI96/00502

7

is generally about 30 W/mK. Tool steel is easy to machine and also hard enough, thus making it very wear resistant. The coating may be e.g. of beryllium copper alloy whose thermal conductivity is about 200 W/mK or more. By means of this coating, the friction heat caused by friction between the plastic material and the tool 2 may be efficiently conducted away from the interface of the plastic material to be extruded and the tool towards the tool 2. It has also been found in tests that then the temperature at the interface can be dropped as much as 30°C. On account of the dropped temperature, polytetrafluoroethylene does not wear off as fast as in earlier applications. Because of friction heat, temperature at the interface has earlier risen easily too high for polytetrafluoroethylene, even if the tool were cooled at other parts. The tests showed that even a drop of 10°C in this critical zone reduces wear of polytetrafluoroethylene and thus adds significantly to the service life of the tool. The temperature of the interface can be dropped by using coating, for example, with a thermal conductivity of over 100 W/mK. The tool 2 may also be of a material with a better thermal conductivity than tool steel.

In addition to using a material with good thermal conductivity, the tool can be coated e.g. with a thin chromium polytetrafluoroethylene coating or a so-called diamond like coating (DLC) where the pores are filled with a fluoro compound, such as polytetrafluoroethylene. DLC resists wear very well and the fluoro compound, which fills the pores, reduces friction between the plastic material and the tool 2.

The nozzle 3 has a tempering unit 6 provided with oil circulation, for example. A similar tempering unit 6 has also been arranged to the mandrel 4. By means of the tempering units 6, the temperature of the

WO 97/10940

PCT/FI96/00502

8

nozzle 3 and the mandrel 4 can be controlled as required by passing heat thereto or removing it therefrom.

5 The method and the apparatus according to the invention is in principle suitable for all extrusion that requires accurate adjustment of temperature and good slip characteristics. For example, in the drive of polyethylene foam, very low temperatures have to be used and because of exothermic reaction, heat has to be removed efficiently from the process. In orientation processes, for example, a typical melt flow causes disturbances in the actual orientation stage of molecules and thus it is preferable that the friction between the plastic material and the tool is reduced with polytetrafluoroethylene. High temperature is a particular problem especially when making crosslinked polyethylene pipes. It is especially difficult to use a material with a high molecular weight for making the product. The method and the apparatus according to the invention is also suitable to be used for materials whose average molecular weight is more than 200,000 g/mol.

Figure 2 shows a schematic cross-sectional side view of a second apparatus according to the invention. The numbers in Figure 2 correspond to those of Figure 1. The extruder according to Figure 2 produces a three-layered product whose outer layer 5b and inner layer 5c preferably form a slip agent layer comprising essentially fluoroplastic, such as polytetrafluoroethylene. Because of these slip agent layers, the extrusion material slips very well along the surface of the tool 2. The coating on the surface of the tool 2, which conducts heat well, causes extra heat to be led efficiently away from the interface, whereby the highest allowed temperature sustainable for

WO 97/10940

PCT/F196/00502

9

the used fluoroplastic will not be exceeded. More preferably, the outer layer 5b and the inner layer 5c comprise at least partly a fluoro compound, such as fluoroelastomer, which is supplied into the plastic, and which migrates to the abutment surfaces of the tool 2 and reduces friction. Differing from the appended figure, the outer layer 5b and the inner layer 5c can be considerably thinner than the middle layer 5a, whereby they form an outer skin and inner skin of the pipe 5. Therefore the slip agent can only be used for thin skins and the effect of the slip agent does not disturb the machining of the material in a middle layer 5a. The middle layer 5a may be crosslinked polyethylene that is difficult to machine.

Figure 3 shows a schematic cross-sectional side view of a third apparatus according to the invention. The numbers in Figure 3 correspond to those of Figures 1 and 2. The extruder contains a first supply channel 7a and a second supply channel 7b, by means of which the outer layer 5b and the inner layer 5c can be supplied to the outside and inside of the middle layer 5a of the extrusion material. The supply channels 7a and 7b are arranged to supply a slip agent layer containing fluoroelastomer or fluoroplastic to the outside and inside of the extrusion material just before the tool 2. In that case, the middle layer 5a can be melted and machined in the extruder portion 1 by using the effect of friction heat very efficiently, as the slip agent layers are supplied to the extruder after plastic melting zone. In Figure 3 the second supply channel 7b is arranged inside the feed screw but it can also be arranged to supply the material from outside through the middle layer 5a. However, forming of a joining seam can be avoided by the solution of Figure 3.

WO 97/10940

PCT/FI96/00502

10

In case the flow of the extrusion material changes so that pure friction flow changes in part into melt flow, transverse stripes are formed in the product, that is, a pattern repeated regularly at distances from about less than a millimetre to some millimetres can be detected in the product. This pattern may not necessarily be visible. In microscopic measurings these transverse stripes can be detected. When handling measuring result mathematically by Fourier analysis, it has been detected that unevenness occurs at regular distances, the distance generally varying between from about less than one millimetre to some millimetres. The method and apparatus of the invention makes the extrusion product slip evenly on the surface of the tool, wherefore unevenness cannot be seen essentially on the surface of the extrusion product.

Figure 4a shows a result of a microscopic measuring from a surface of an unsatisfactory pipe. On X axle the outer surface of the pipe is on a profilometer and the coarseness of the pipe is on Y axle. The unevenness visible in the figure is not necessary visible for the naked eye, but as can be seen in the appended figure, unevenness can be clearly detected in microscopic measuring.

Figure 4b shows a Fourier analysis of measuring according to Figure 4a. Sequentiality of unevenness can be clearly detected in the Fourier analysis, a sequence being 0.81 mm at wave length. Finding a specific wave length proves that the flow of the plastic material is not steady, but pure friction flow has partly changed into melt flow.

Figure 5a shows a microscopic measuring of a pipe made with the method according to the invention. It can be seen in Figure 5a that the surface has been

WO 97/10940

PCT/FI96/00502

11

fairly even. A Fourier analysis shown in Figure 5b is also made of the measuring of Figure 5a and it proves that now sequential unevenness cannot be detected.

5 The drawing and the specification related thereto are only intended to illustrate the idea of the invention. In its details the invention may vary within the scope of the claims.

WO 97/10940

PCT/FI96/00502

12

Claims

1. A method for making an extrusion product, in which method an extrusion material is extruded by an extruder from its extrusion portion (1) through a tool (2) and fluoropolymer is used between the extrusion material and the tool (2) for reducing friction between the extrusion material and the tool, characterized in that at least the surface of the tool (2) against fluoropolymer is of a material whose thermal conductivity is greater than the thermal conductivity of ordinary tool steel, whereby the friction heat generated can be conducted efficiently away from the interface between the tool (2) and the extrusion material towards the tool (2).

2. A method according to claim 1, characterized in that the temperature of the tool is adjusted as required with a tempering unit (6).

3. A method according to claim 1 or 2, characterized in that the extrusion product is a product with at least two layers and that the layer against the tool (2) comprises at least partly a fluoro compound which is supplied into the plastic, and which migrates to the abutment surfaces of the tool (2).

4. A method according to any one of the preceding claims, characterized in that the extrusion product is a plastic pipe (5) with at least three layers comprising an outer skin and an inner skin, whereby the outer skin and the inner skin comprise at least partly a fluoro compound, such as fluoroelastomer, which is supplied into the plastic, and which migrates to the abutment surfaces, and that a middle layer (5a) of the pipe (5) is essentially of a material that does not contain a slip agent.

WO 97/10940

PCT/FI96/00502

13

5. A method according to any one of the preceding claims, characterized in that a slip agent containing fluoroelastomer or fluoroplastic is extruded between the plastic material to be extruded and the tool (2) primarily after plastic melting zone before the tool (2).

6. A method according to any one of the preceding claims, characterized in that the thermal conductivity of at least the surface of the tool (2) against fluoropolymer is greater than 100 W/mK.

7. A method according to any one of the preceding claims, characterized in that the thermal conductivity of at least the surface of the tool (2) against fluoropolymer is greater than 200 W/mK.

8. A method according to claim 7, characterized in that at least the surface of the tool (2) against fluoropolymer is of beryllium copper alloy.

9. A method according to any one of the preceding claims, characterized in that a plastic material with an average molecular weight of more than 200,000 g/mol is used as the extrusion material.

10. A method according to any one of the preceding claims, characterized in that the extrusion product is a crosslinked polyethylene pipe (5).

11. An apparatus for making an extrusion product, which apparatus comprises an extrusion portion (1) for extruding an extrusion material and a tool (2) through which the extrusion material is extruded and fluoropolymer is arranged to be used between the extrusion material and the tool (2) as a slip agent, characterized in that at least the surface

WO 97/10940

PCT/FI96/00502

14

of the tool (2) against fluoropolymer, at least partly at the smallest cross section, is of a material whose thermal conductivity is greater than the thermal conductivity of ordinary tool steel.

5 12. An apparatus according to claim 11, characterized in that the tool (2) comprises a tempering unit (6) for controlling the temperature of the tool (2).

10 13. An apparatus according to claim 11 or 12, characterized in that at least in some places the surface of the tool comprises in the axial direction a chrome polytetrafluoroethylene coating or DLC where pores have been filled with a fluoro compound.

15 14. An apparatus according to any one of claims 11 to 13, characterized in that the apparatus has been arranged to make a three-layered product.

20 15. An apparatus according to claim 14, characterized in that the apparatus comprises means for extruding a slip agent containing fluoroelastomer or fluoroplastic between the plastic material to be extruded and the tool (2) primarily after plastic melting zone before the tool (2).

25 16. An apparatus according to any one of claims 10 to 15, characterized in that the thermal conductivity of at least the surface of the tool (2) against fluoropolymer is greater than 100 W/mK.

30 17. An apparatus according to claim 16, characterized in that at least the surface of the tool (2) against fluoropolymer is of beryllium copper alloy whose thermal conductivity is more than 200 W/mK.

35 18. A product made with the method according

WO 97/10940

PCT/FI96/00502

15

to claim 1, characterized in that the surface of the product is essentially smooth without transverse microscopic stripes repeated at a specific wave length.

5 19. A product according to claim 18, characterized in that the product is a pipe (5) comprising at least three layers (5a, 5b, 5c), whereby at least the outer and inner layers (5b, 5c) comprise a slip agent containing a fluoro compound.

10 20. A product according to claim 19, characterized in that thin skins form the outer and inner layer (5b, 5c).

 21. A product according to claim 19 or 20, characterized in that the middle layer
15 (5a) comprises a material whose average molecular weight is more than 200,000 g/mol.

 22. A product according to claim 21, characterized in that the middle layer (5a)
20 primarily comprises essentially crosslinked polyethylene that does not contain a slip agent.

WO 97/10940

PCT/FI96/00502

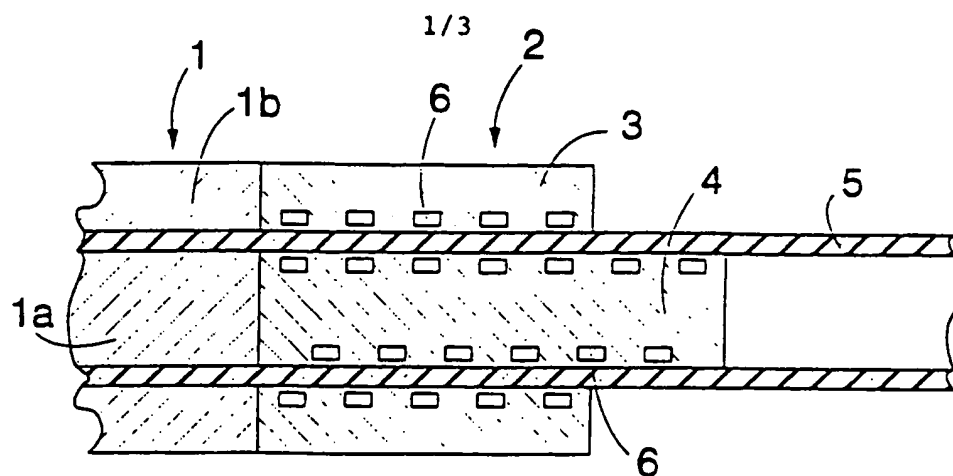


FIG. 1

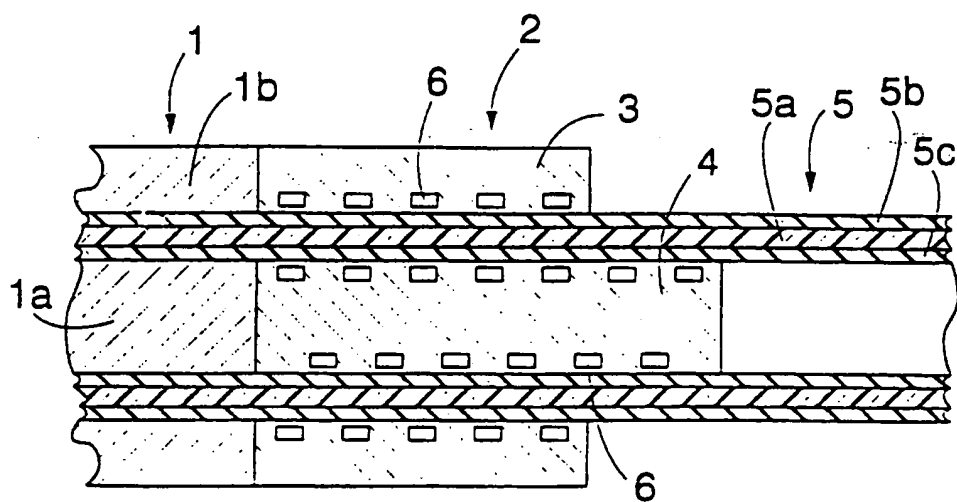


FIG. 2

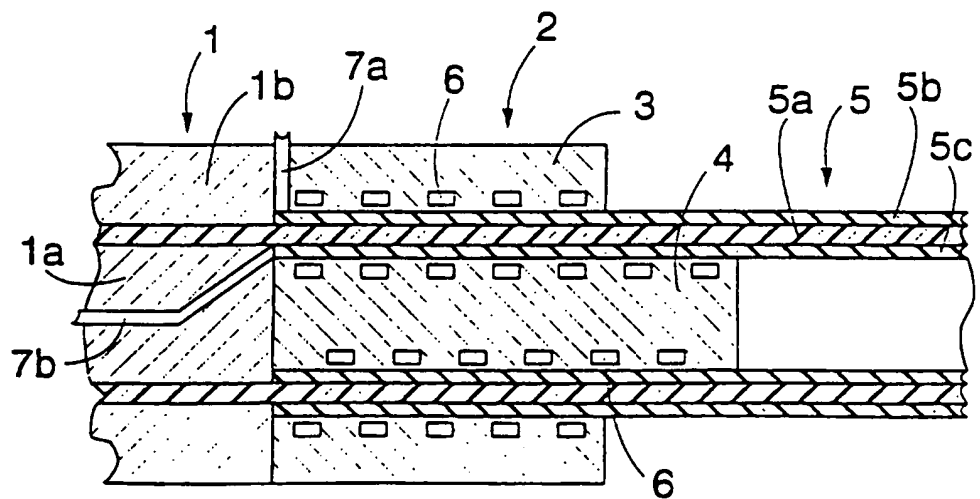


FIG. 3

WO 97/10940

PCT/FI96/00502

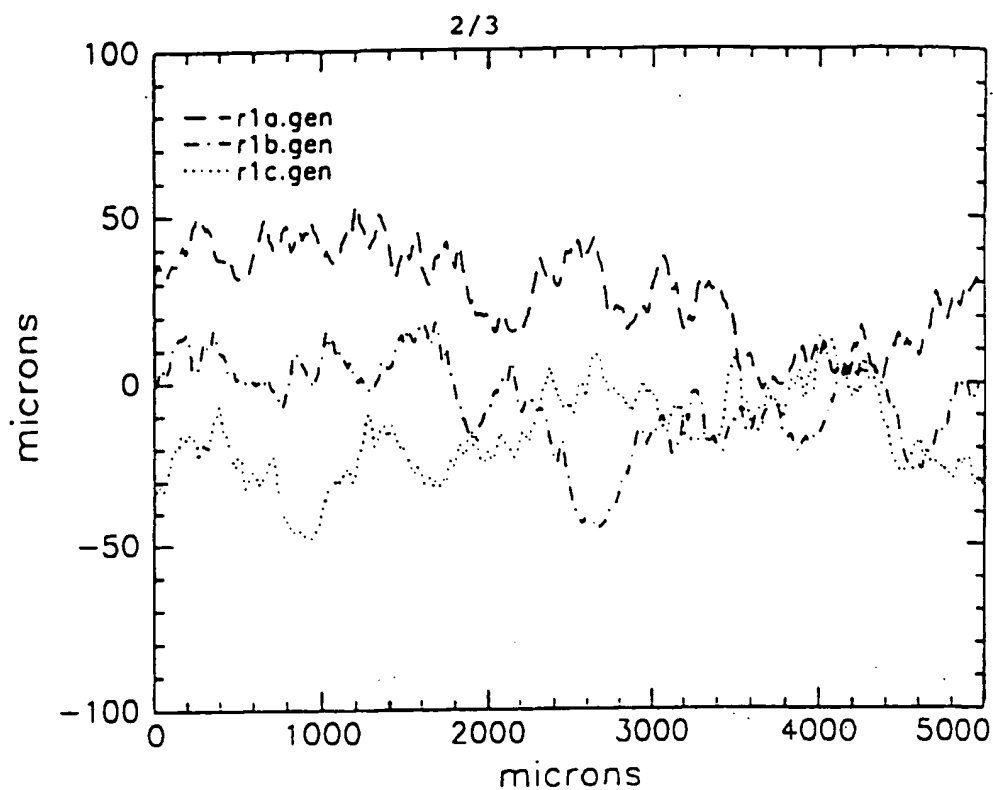


FIG. 4a

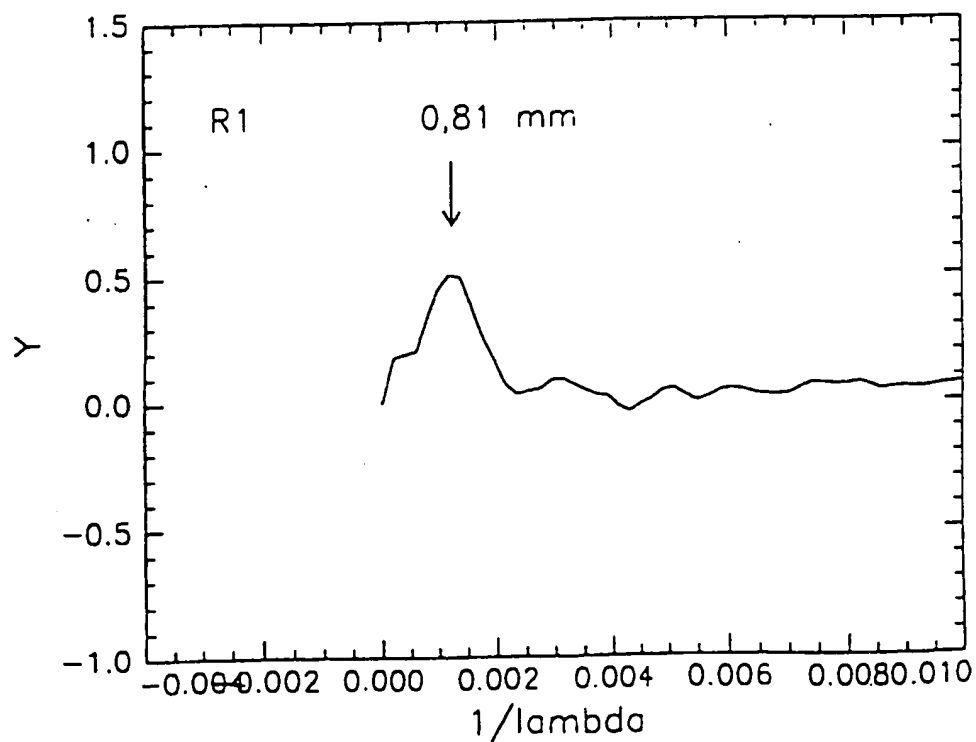


FIG. 4b

WO 97/10940

PCT/F196/00502

3/3

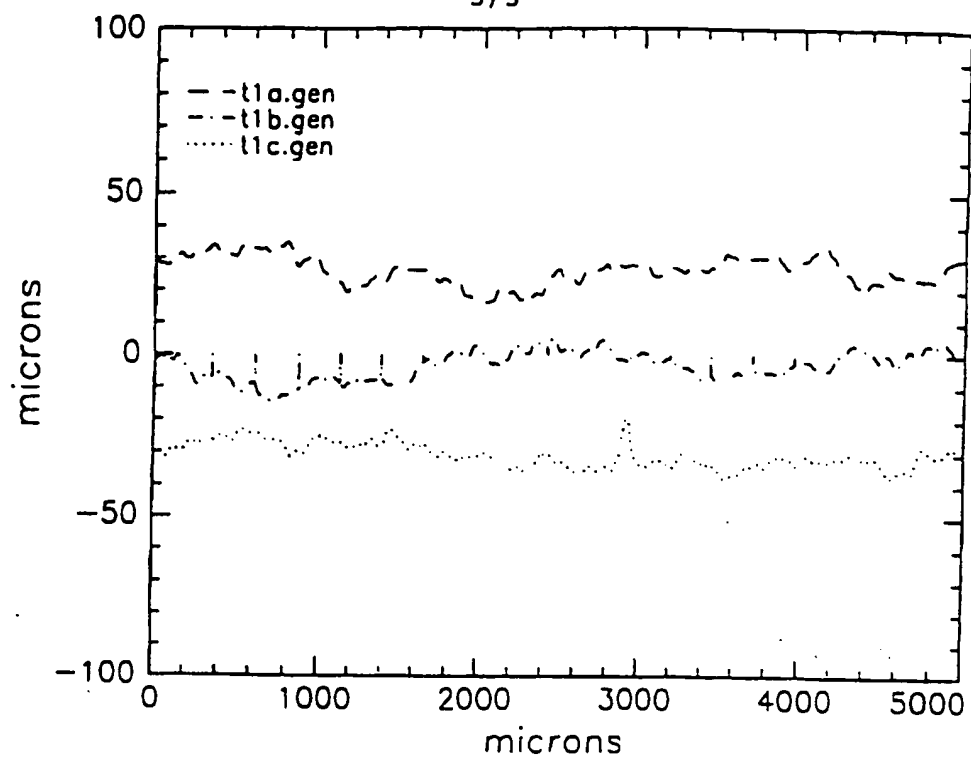


FIG. 5a

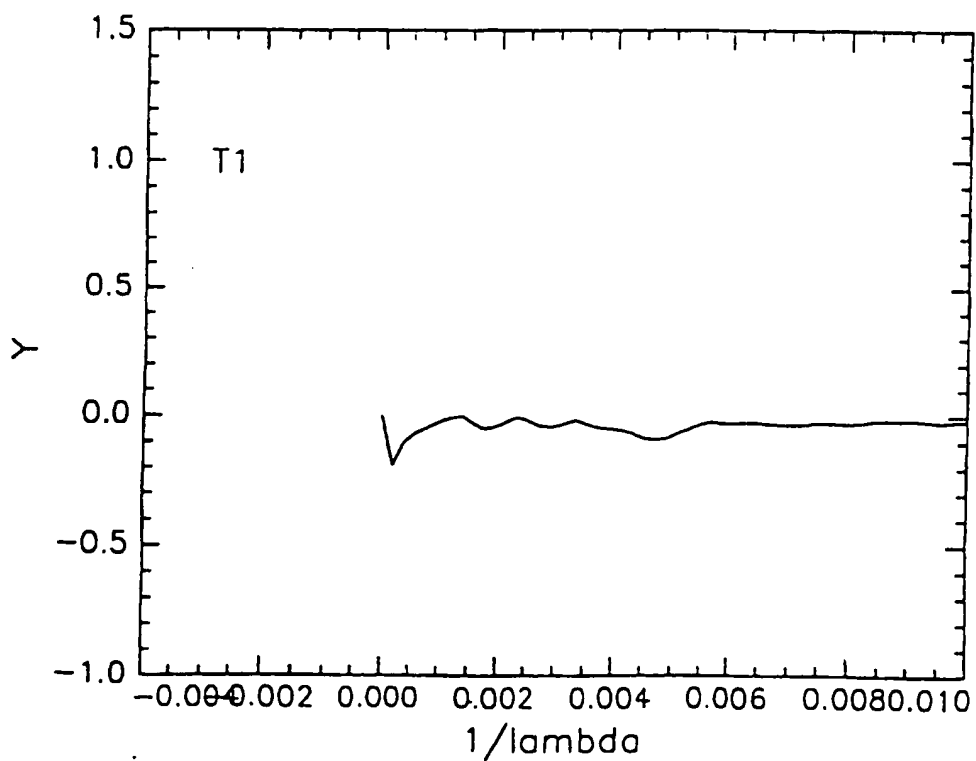


FIG. 5b

INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 96/00502

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: B29C 47/88

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: B29C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0507613 A2 (MITSUI PETROCHEMICAL INDUSTRIES, LTD.), 7 October 1992 (07.10.92), page 7, line 49 - line 52; page 12, line 51 - line 52 --	1, 11, 18
A	WO 9219809 A1 (SULZER-ESCHER WYSS GMBH), 12 November 1992 (12.11.92), page 3, line 22 - line 31 --	1-22
A	DE 4412799 A1 (HOECHST AG), 19 October 1995 (19.10.95), column 3, line 49 - line 55, claims 1-9, abstract -- -----	1-22

☐ Further documents are listed in the continuation of Box C.
 ☒ See patent family annex.

- * Special categories of cited documents
- *A* document defining the general state of the art which is not considered to be of particular relevance
 - *E* earlier document but published on or after the international filing date
 - *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
 - *O* document referring to an oral disclosure, use, exhibition or other means
 - *P* document published prior to the international filing date but later than the priority date claimed
 - *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
 - *X* document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
 - *Y* document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
 - *Z* document member of the same patent family

Date of the actual completion of the international search

17 December 1996

Date of mailing of the international search report

09 -01- 1997

Name and mailing address of the ISA/

 Swedish Patent Office
 Box 5055, S-102 42 STOCKHOLM
 Facsimile No. +46 8 666 02 86

Authorized officer

 Britt-Marie Lundell
 Telephone No. +46 8 782 25 00

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/FI 96/00502

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A2- 0507613	07/10/92	CA-C- 2064939	01/08/95
		JP-A- 4305432	28/10/92
		KR-B- 9505729	29/05/95
		US-A- 5290498	01/03/94
		US-A- 5417561	23/05/95
		JP-A- 4312841	04/11/92
		JP-A- 4357012	10/12/92
WO-A1- 9219809	12/11/92	AT-T- 143429	15/10/96
		CA-A- 2086007	04/11/92
		CH-A- 682893	15/12/93
		DE-A,C- 4125613	05/11/92
		DE-A- 4126232	12/11/92
		DE-D- 59207239	00/00/00
		EP-A,B- 0537315	21/04/93
		IT-B- 1255300	31/10/95
		IT-D- MI920999	00/00/00
		US-A- 5240666	31/08/93
		US-A- 5393290	28/02/95
DE-A1- 4412799	19/10/95	NONE	

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☒ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER: _____**

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.